

# **ATMOSPHERIC CHEMISTRY OF ALKANES**

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## **ATMOSPHERIC CHEMISTRY OF SELECTED LINEAR, BRANCHED AND CYCLIC C<sub>10</sub> ALKANE COMPONENTS OF MINERAL SPIRITS**

California Air Resources Board Contract No. 97-312

August 9, 2002

- Alkanes are important components of gasoline (comprising ~60% of gasoline) and vehicle exhaust, and account for ~40% of non-methane organic compounds in urban atmospheres.
- C<sub>9</sub>-C<sub>13</sub> alkanes are important constituents of mineral spirits.

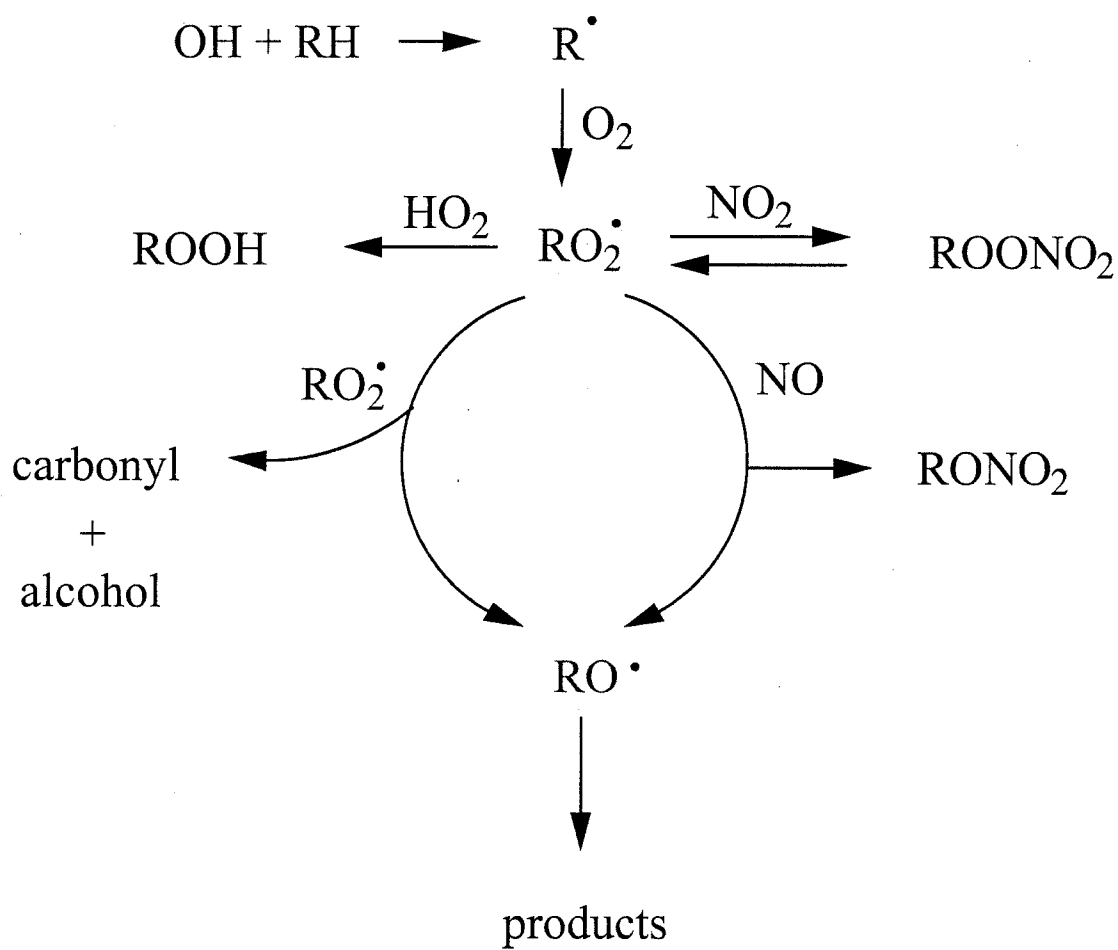
In the atmosphere, alkanes react with:

- OH radicals during daylight hours.
- NO<sub>3</sub> radicals during nighttime hours.
- Cl atoms in coastal areas.

Reaction with OH radicals is estimated to dominate over reaction with NO<sub>3</sub> radicals, by a factor of ~100.

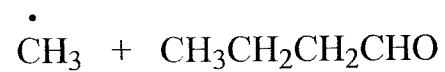
<b>Alkane</b>	<b>Lifetime</b>
Ethane	50 days
Propane	10 days
<i>n</i> -Butane	5 days
<i>n</i> -Decane	1 day

Alkanes react by H-atom abstraction from the various C-H bonds:

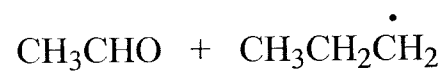




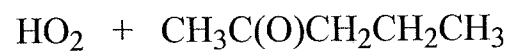
decomposition



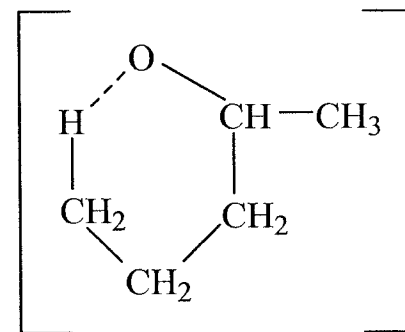
or

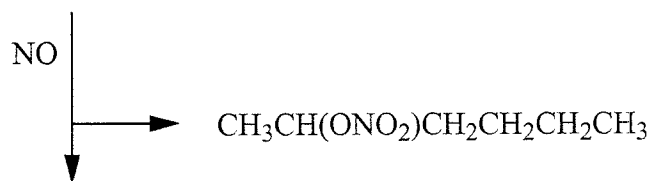
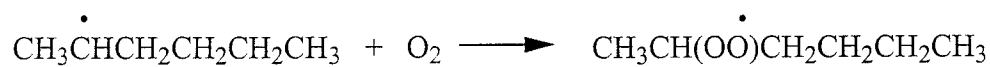


$\text{O}_2$

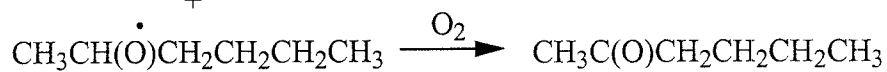


isomerization





+

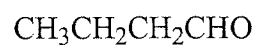
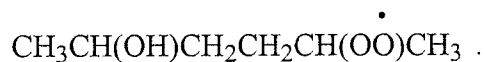


+

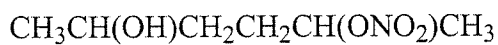
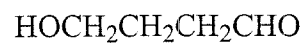


isomerization

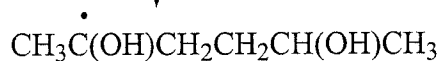
decomposition



and



isomerization



As of approximately 1995, the only products identified (and quantified) were carbonyl compounds arising from alkoxy radical decomposition and reaction with O<sub>2</sub>:

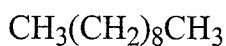
alkane	yield (%)	
	carbonyls	alkyl nitrates
<i>n</i> -butane	89	7.7
<i>n</i> -pentane	47	10.5
<i>n</i> -hexane	10	21
<i>n</i> -heptane	≤1	31
<i>n</i> -octane	≤1	33

Hydroxycarbonyls have since been observed by:

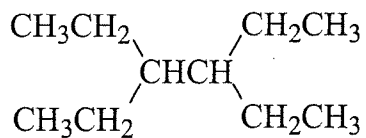
- Eberhard *et al.* (1995) from *n*-hexane, derivatizing the carbonyl group with DNPH and analysis by GC-MS.
- Atkinson *et al.* (1995) from *n*-pentane, and Kwok *et al.* (1996) from *n*-butane through *n*-octane, using *in situ* API-MS

## PROJECT GOALS

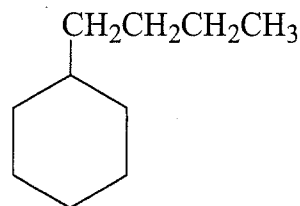
The goal of this contract was to investigate the atmospheric chemistry (lifetime and products) of three C<sub>10</sub> alkanes which were representative of those in mineral spirits.



*n* -Decane



2,3-Diethylhexane

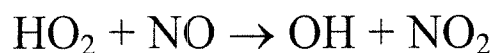
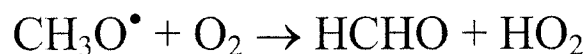
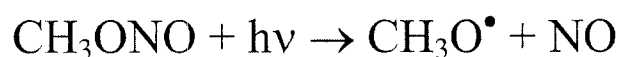


*n* -Butylcyclohexane

The first part of the project involved development of analytical methods to identify and quantify hydroxycarbonyls and hydroxynitrates from *n*-pentane through *n*-octane, as well as a re-determination of the alkyl nitrate formation yields from these *n*-alkanes.

## EXPERIMENTAL APPROACH

- Experiments were carried out in ~7000 liter Teflon chambers, with blacklight irradiation, in purified air at ~5% relative humidity.
- OH radicals were generated by photolysis of methyl nitrite in air:

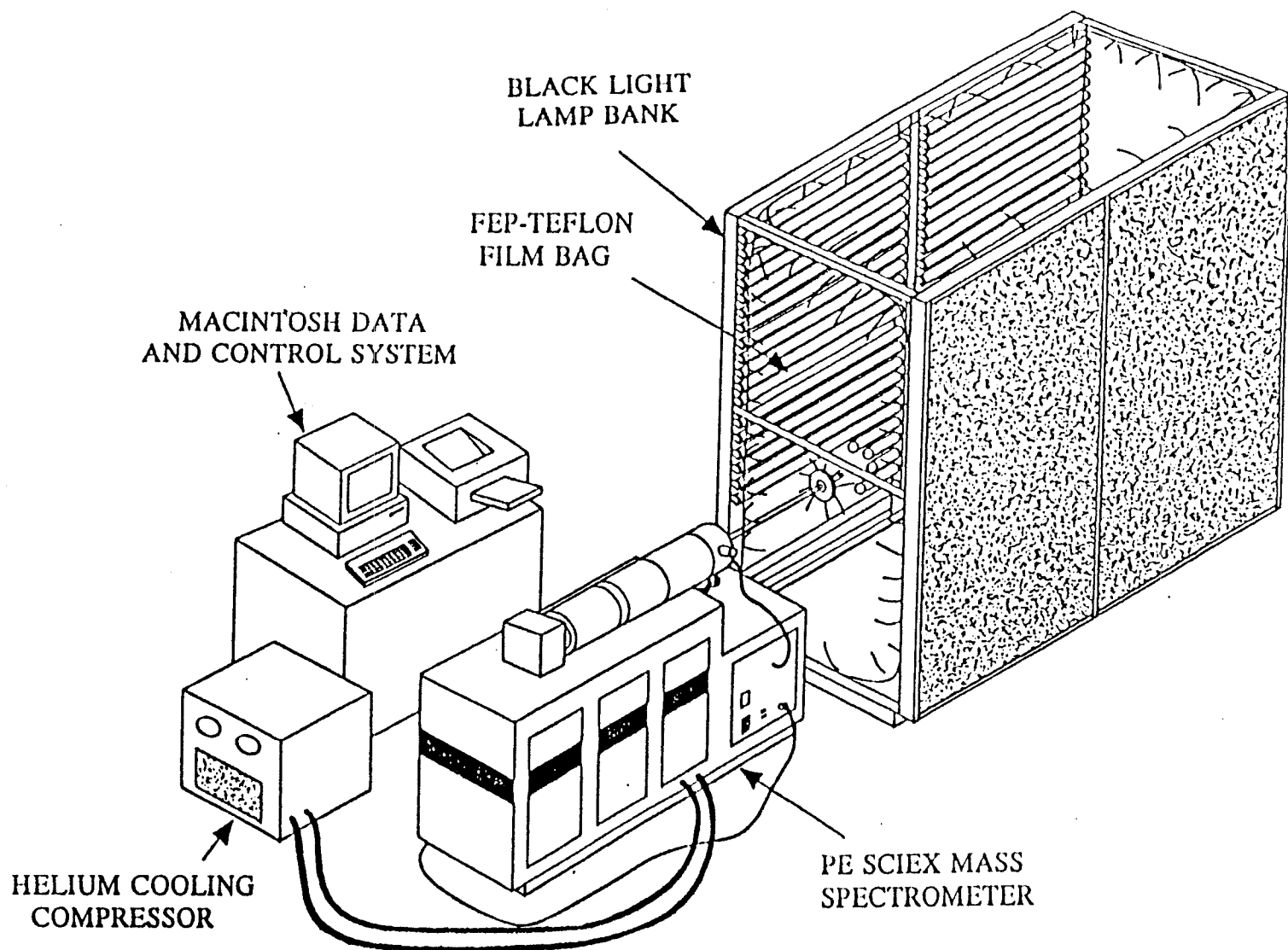


- Analyses were by GC-FID (solid adsorbent/thermal desorption) or by API-MS.

Initial concentrations (molecule  $\text{cm}^{-3}$ ) were

$\text{CH}_3\text{ONO}$  and  $\text{NO}$ , equal at  $(0.24-24) \times 10^{13}$  (0.1-10 ppm)

Alkane,  $(0.24-2.4) \times 10^{13}$  (0.1-1 ppm)



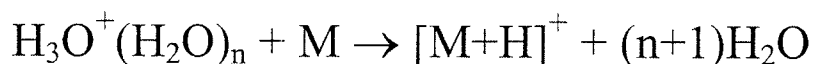
APRC PE SCIEX API III MS/MS

## C<sub>5</sub>-C<sub>8</sub> *n*-alkanes

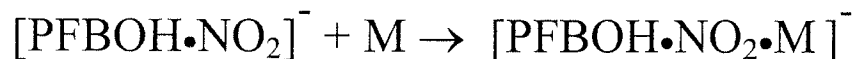
- Measurement of alkyl nitrate yields (*e.g.*, 2- and 3-pentyl nitrates from *n*-pentane) using GC-FID analyses.
- Identification and quantification of hydroxycarbonyls and hydroxynitrates (*e.g.*, hydroxypentanones and hydroxypentyl nitrates from *n*-pentane) using API-MS and API-MS/MS analyses.

## API-MS analyses

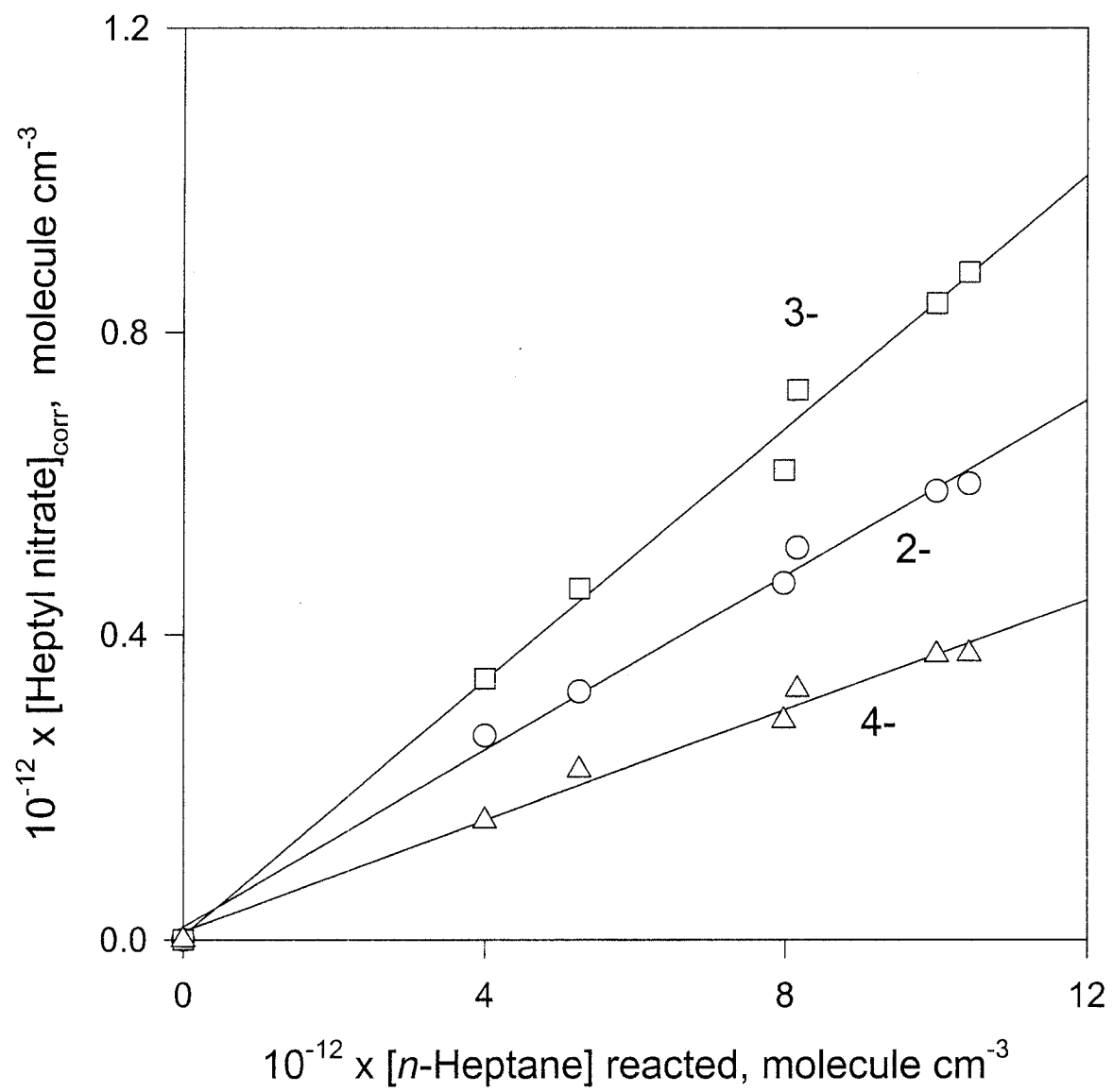
- Previously [Atkinson *et al.* (1995) and Kwok *et al.* (1996)] we had used the API-MS in positive ion mode, with protonated water clusters as the reagent ion:



- In this study, we investigated the use of  $\text{O}_2^-$ ,  $\text{NO}_2^-$ ,  $[\text{PFBOH}\cdot\text{O}_2]^-$  and  $[\text{PFBOH}\cdot\text{NO}_2]^-$  as the reagent ions, where  $\text{PFBOH} = \text{C}_6\text{F}_5\text{CH}_2\text{OH}$ , resulting in the formation of adduct ions:



*etc.*



## Alkyl nitrate yields

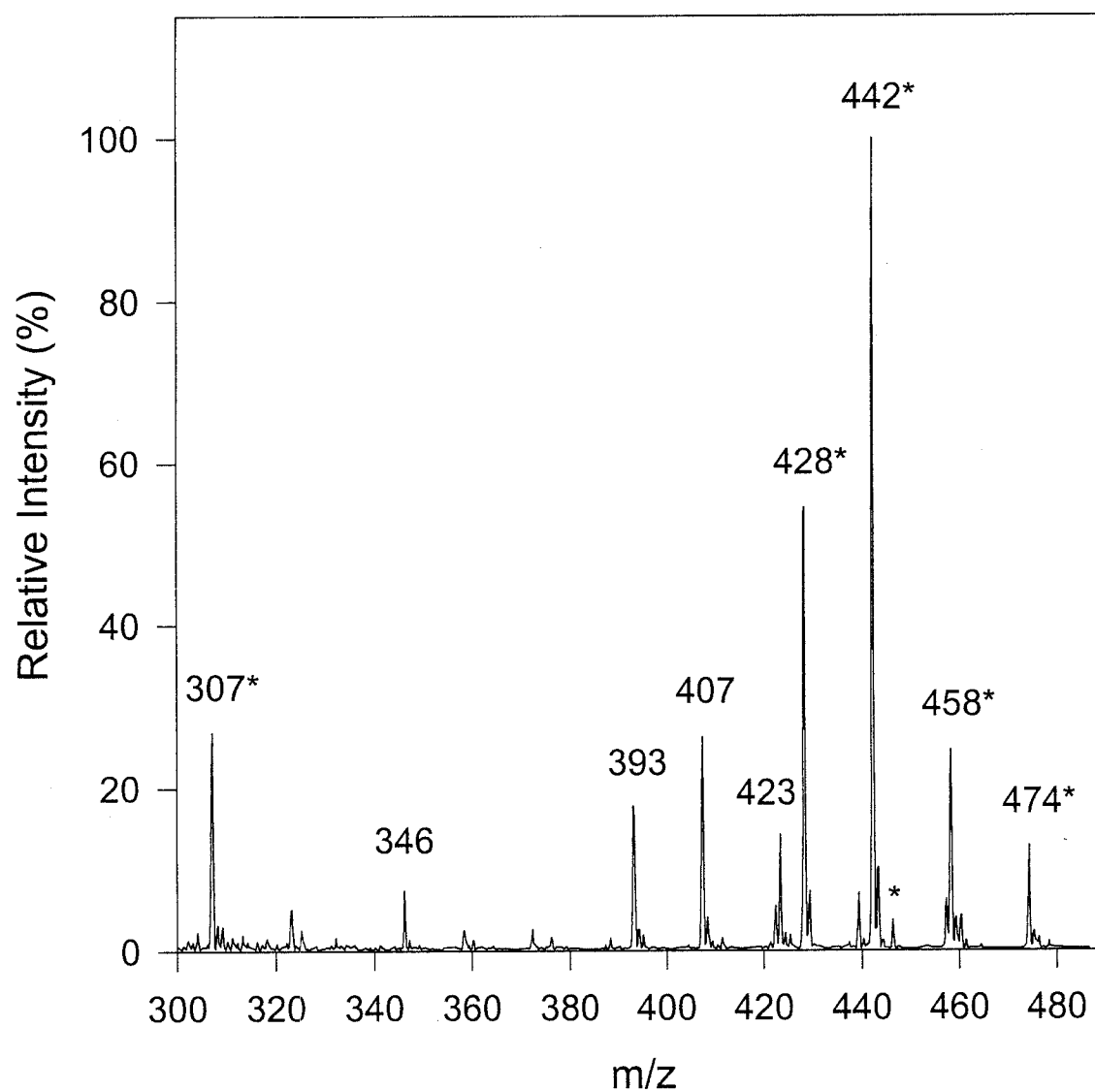
Alkane	Formation yield (%)		
	2-nitrate	3-nitrate	4-nitrate
<i>n</i> -pentane	$6.0 \pm 1.0$	$4.4 \pm 0.6$	
<i>n</i> -hexane	$5.9 \pm 0.7$	$8.2 \pm 1.0$	
<i>n</i> -heptane	$5.9 \pm 0.6$	$8.3 \pm 0.9$	$3.6 \pm 0.5$
<i>n</i> -octane	$6.2 \pm 0.6$	$8.1 \pm 0.8$	$8.3 \pm 1.2$

Alkane	Total alkyl nitrate yield (%)	
	previous work	this work
ethane	$\leq 1.4$	
propane	$3.6 \pm 0.5$	
<i>n</i> -butane	$7.7 \pm 0.5$	
<i>n</i> -pentane	$11.7 \pm 1.3$	$10.5 \pm 1.4$
<i>n</i> -hexane	$20.8 \pm 2.7$	$14.1 \pm 2.0$
<i>n</i> -heptane	$29.3 \pm 4.2$	$17.8 \pm 2.4$
<i>n</i> -octane	$31.8 \pm 2.7$	$22.6 \pm 3.2$

## API-MS analyses

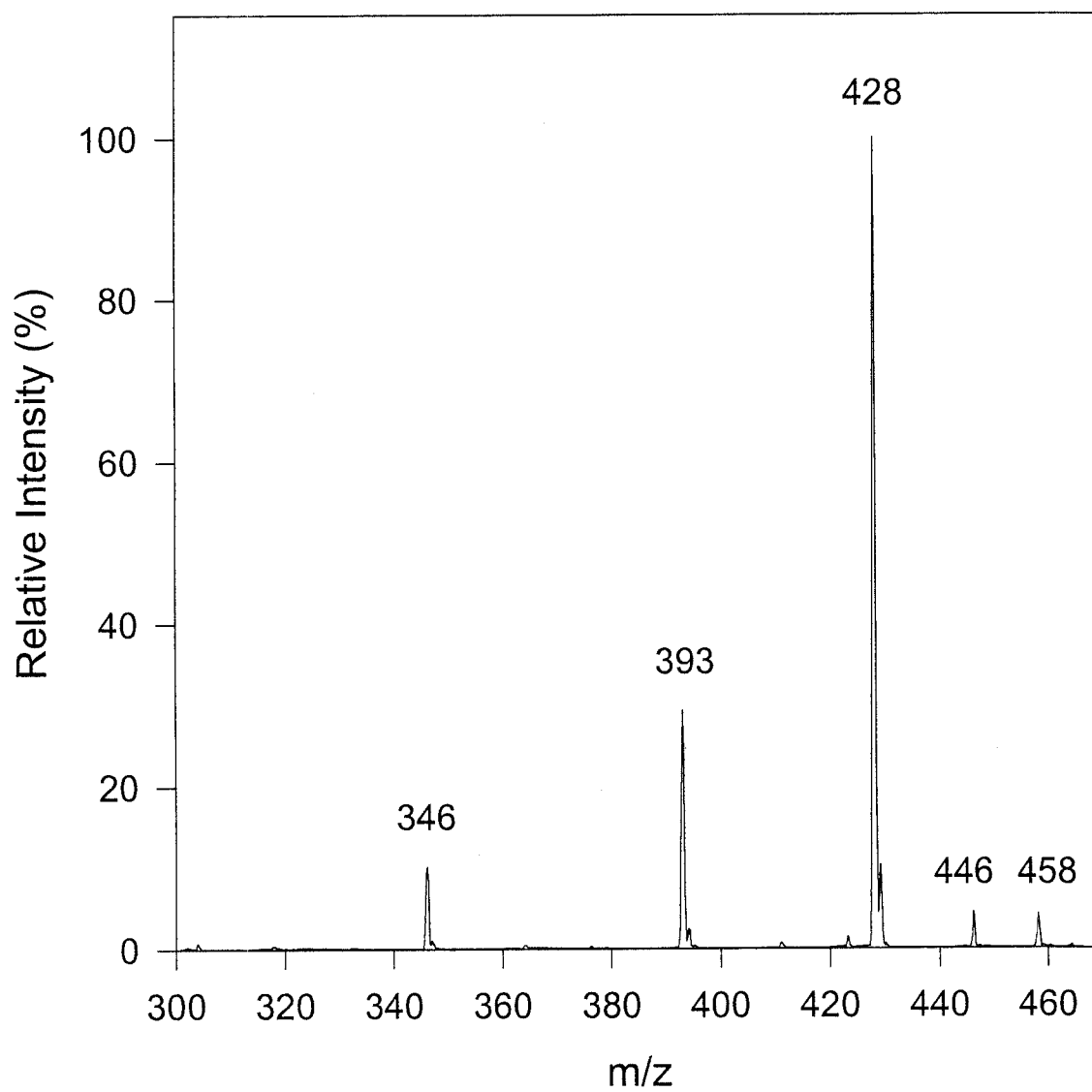
- Our previous 1995 and 1996 studies used the positive ion mode, with protonated water clusters as the reagent ion.
- The C<sub>n</sub>-hydroxycarbonyls from the C<sub>n</sub>-alkane were observed, as the [M+H]<sup>+</sup>, [M-H]<sup>+</sup> and [M+H-H<sub>2</sub>O]<sup>+</sup> ions.
- Because of fragmentation and homo- and hetero-dimer formation, quantification of hydroxycarbonyls did not appear possible.
- Hydroxynitrates were not observed.
- Therefore, in this study we used the negative ion mode, initially using [PFBOH•O<sub>2</sub>]<sup>-</sup> to form adduct ions.

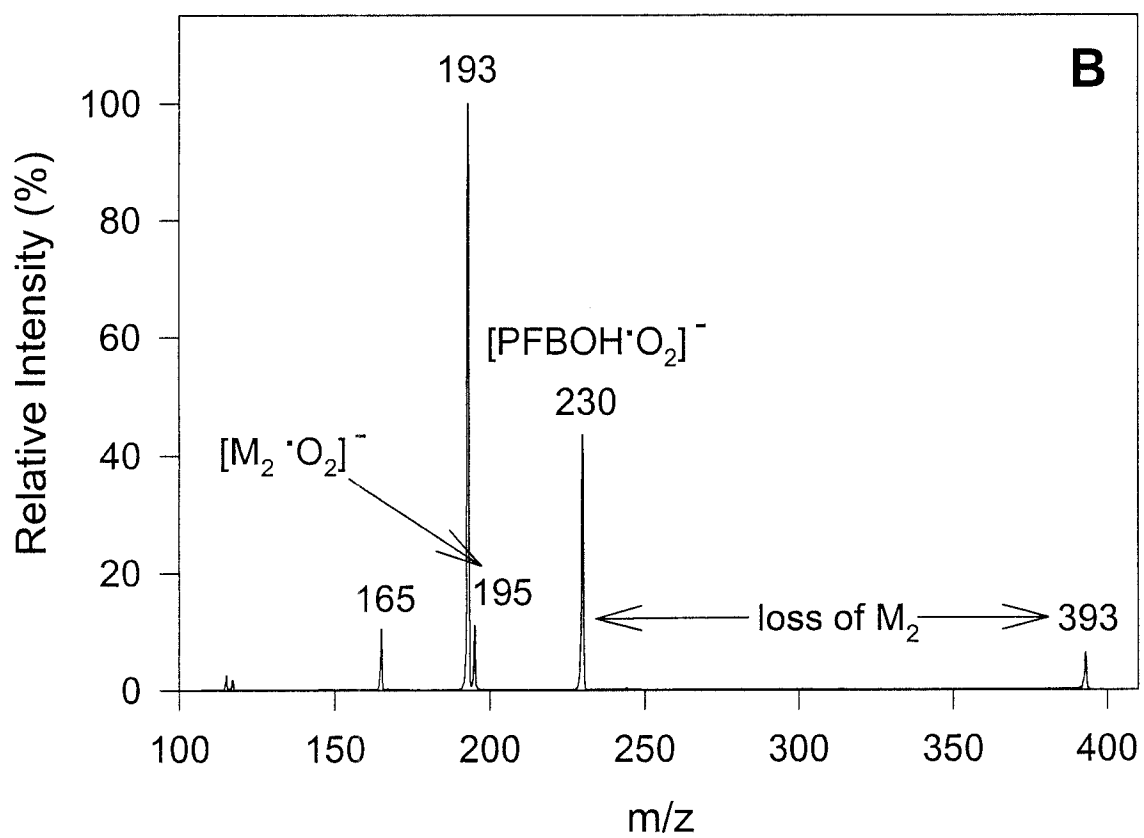
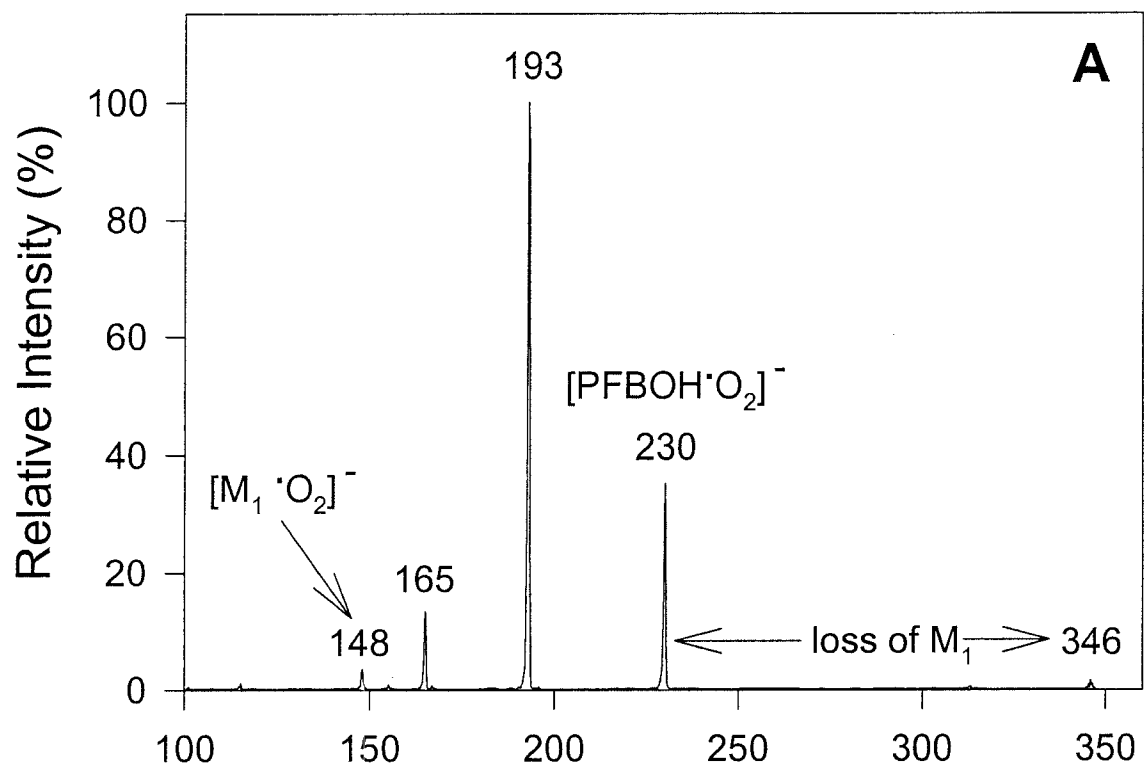
API-MS spectrum of OH + *n*-hexane reaction,  
with addition of PFBOH to the sampled air stream



- Clearly, there are  $[\text{PFBOH}\cdot\text{NO}_2]^-$  and  $[\text{PFBOH}\cdot\text{O}_2\cdot\text{NO}]^-$  present as well as  $[\text{PFBOH}\cdot\text{O}_2]^-$ , and these also form adducts with products.
- The presence of  $[\text{PFBOH}\cdot\text{O}_2\cdot\text{M}]^-$  ions was determined from API-MS/MS “precursor ion” spectra of the 230 u  $[\text{PFBOH}\cdot\text{O}_2]^-$  ion, and confirmed from API-MS/MS “fragment ion” spectra of the  $[\text{PFBOH}\cdot\text{O}_2\cdot\text{M}]^-$  ions.

OH + *n*-hexane: API-MS/MS precursor ion  
spectrum of the 230 u [PFBOH.O<sub>2</sub>]<sup>-</sup> ion





Products M observed from the presence of  $[\text{PFBOH}\cdot\text{O}_2\cdot\text{M}]^-$

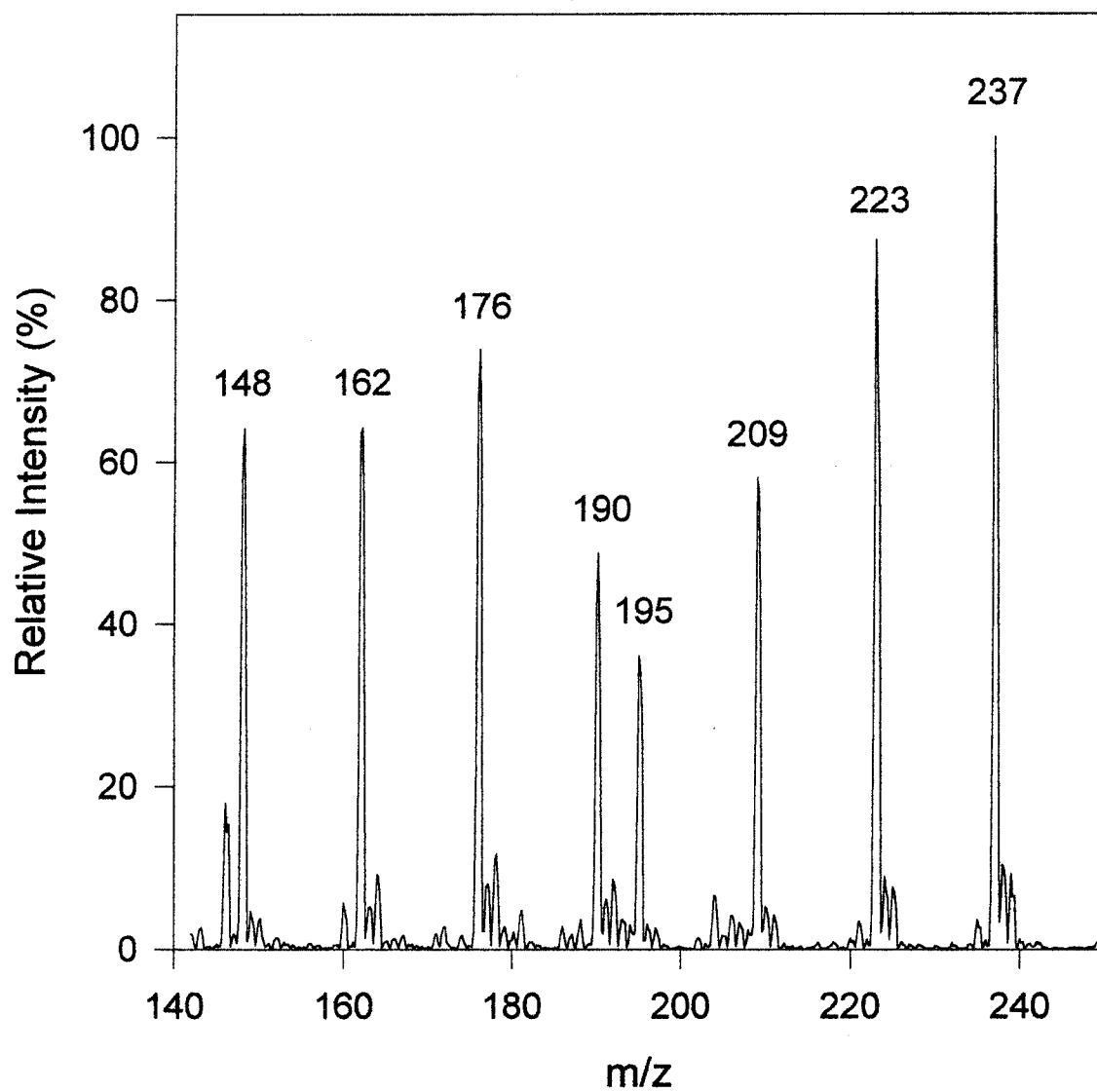
ions. -OD groups rapidly undergo -OD to -OH exchange:

$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  and  $\text{CD}_3\text{C}(\text{O})\text{CD}_2\text{CD}_2\text{CD}_2\text{OH}$

Alkane	Molecular weight of product M	
	alkane- $\text{h}_{2n+2}$	alkane- $\text{d}_{2n+2}$
<i>n</i> -pentane	102	111
	149	159
<i>n</i> -hexane	116	127
	163	175
<i>n</i> -heptane	130	143
	177	191
<i>n</i> -octane	144	159
	191	207

- While this was fine for observation of hydroxycarbonyls and hydroxynitrates,  $\text{NO}_2$  concentrations increased during the  $\text{CH}_3\text{ONO} - \text{NO} - \text{alkane} - \text{air}$  irradiations and  $[\text{PFBOH}\cdot\text{NO}_2]^-$  competed with  $[\text{PFBOH}\cdot\text{O}_2]^-$  for adduct formation, making quantification very difficult.
- We finally concluded that quantification of hydroxycarbonyls and hydroxynitrates as their  $\text{NO}_2^-$  adducts was the best strategy, and with  $\text{NO}_2$  concentrations  $\sim 2.4 \times 10^{13} \text{ molecule cm}^{-3}$  (1 ppm) to ensure that  $[\text{NO}_2\cdot\text{M}]^-$  dominated over  $[\text{O}_2\cdot\text{M}]^-$ .

$\text{NO}_2^-$  adducts, OH radical-initiated reaction of  
*n*-pentane, *n*-hexane, *n*-heptane and *n*-octane



- A series of OH + C<sub>5</sub>-C<sub>8</sub> *n*-alkane reactions were carried out with differing relative initial alkane concentrations, resulting in relative formation yields of hydroxycarbonyls and of hydroxynitrates.
- For individual OH + *n*-alkane reactions, internal standards were added/formed in the chamber: 5-hydroxy-2-pentanone was added after the reactions for hydroxycarbonyl quantification, and CH<sub>3</sub>CH(OH)CH(ONO<sub>2</sub>)CH<sub>3</sub> was formed *in situ* from OH + *cis*-2-butene (3.5% yield) for quantification of hydroxynitrates.

### Hydroxycarbonyl yields

	<i>n</i> -pentane	<i>n</i> -hexane	<i>n</i> -heptane	<i>n</i> -octane
Relative	$1.33 \pm 0.67$	$1.97 \pm 0.61$	$1.69 \pm 0.29$	1.00
vs standard	60%	49%	29%	24%
Yield	36%	53%	46%	27%

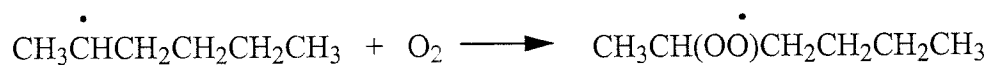
### Hydroxynitrate yields

	<i>n</i> -pentane	<i>n</i> -hexane	<i>n</i> -heptane	<i>n</i> -octane
Relative	$0.48 \pm 0.12$	$0.85 \pm 0.20$	$0.87 \pm 0.05$	1.00
vs standard	2.4%	4.6%	4.8%	5.6%
Yield	2.6%	4.6%	4.7%	5.4%

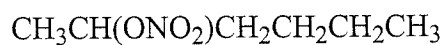
Product yields (%)

	<i>n</i> -pentane	<i>n</i> -hexane	<i>n</i> -heptane	<i>n</i> -octane
Carbonyls	47	10	≤1	≤1
Nitrates	10.5	14.1	17.8	22.6
Hydroxycarbonyls	36	53	46	27
Hydroxynitrates	2.6	4.6	4.7	5.4
Total	96 <sup>+40</sup> <sub>-20</sub>	82 <sup>+55</sup> <sub>-30</sub>	69 <sup>+50</sup> <sub>-25</sub>	55 <sup>+30</sup> <sub>-15</sub>

If alkoxy radical isomerization can occur, then for the *n*-alkanes isomerization dominates (at room temperature) and formation of hydroxycarbonyls dominates (and products are alkyl nitrates, hydroxycarbonyls and hydroxynitrates).

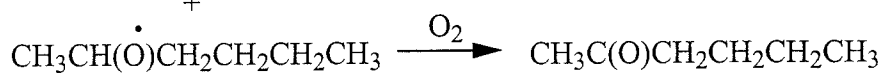


NO



NO<sub>2</sub>

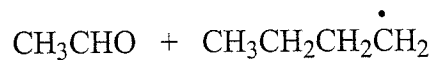
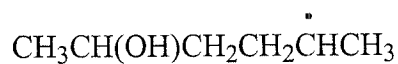
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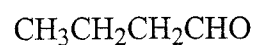
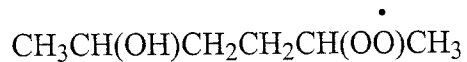
+  
HO<sub>2</sub>

isomerization

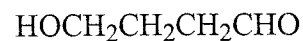
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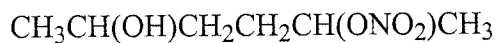
O<sub>2</sub>



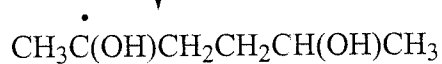
and



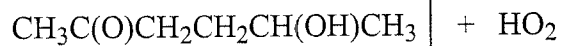
NO



isomerization



O<sub>2</sub>



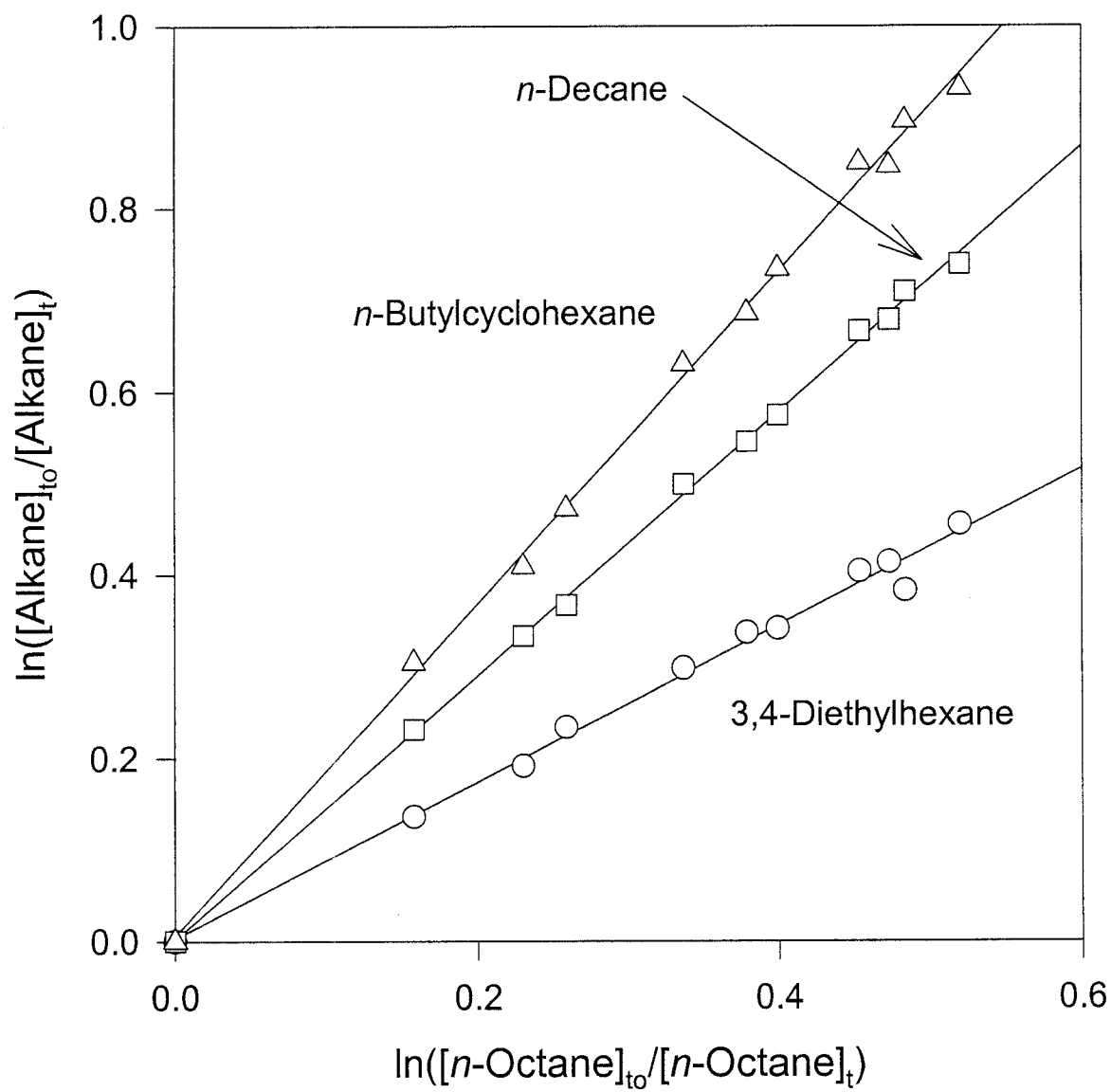
## **C<sub>10</sub> Alkanes**

- Rate constants for their reaction with OH radicals were measured using a relative rate method.
- Carbonyl and alkyl nitrate products were analyzed by GC-FID and confirmed by GC-MS.
- Hydroxycarbonyls and hydroxynitrates were identified and quantified by API-MS in negative ion mode using  $\text{NO}_2^-$  to form adducts, with internal standards.
- API-MS analyses also used the positive ion mode, with protonated water clusters as the reagent ion.

$\text{OH} + \text{C}_{10} \text{ alkane} \rightarrow \text{products} \quad (1)$

$\text{OH} + n\text{-octane} \rightarrow \text{products} \quad (2)$

$$\ln([C_{10}]_{t_0}/[C_{10}]_t) = (k_1/k_2) \ln([n\text{-octane}]_{t_0}/[n\text{-octane}]_t)$$



Room temperature rate constants and lifetimes for the  
reactions of C<sub>10</sub>-alkanes with OH radicals

alkane	10 <sup>12</sup> x k <sub>1</sub> (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )		lifetime (days)
	this work	literature	
<i>n</i> -decane	12.5 ± 0.4	11.1 ± 0.5 <sup>a</sup>  11.1 ± 0.4 <sup>b</sup>  12.4 ± 0.2 <sup>c</sup>	0.9
3,4-diethylhexane	7.43 ± 0.48		1.6
<i>n</i> -butylcyclohexane	15.8 ± 0.6		0.7

<sup>a</sup>Atkinson *et al.* (1982).

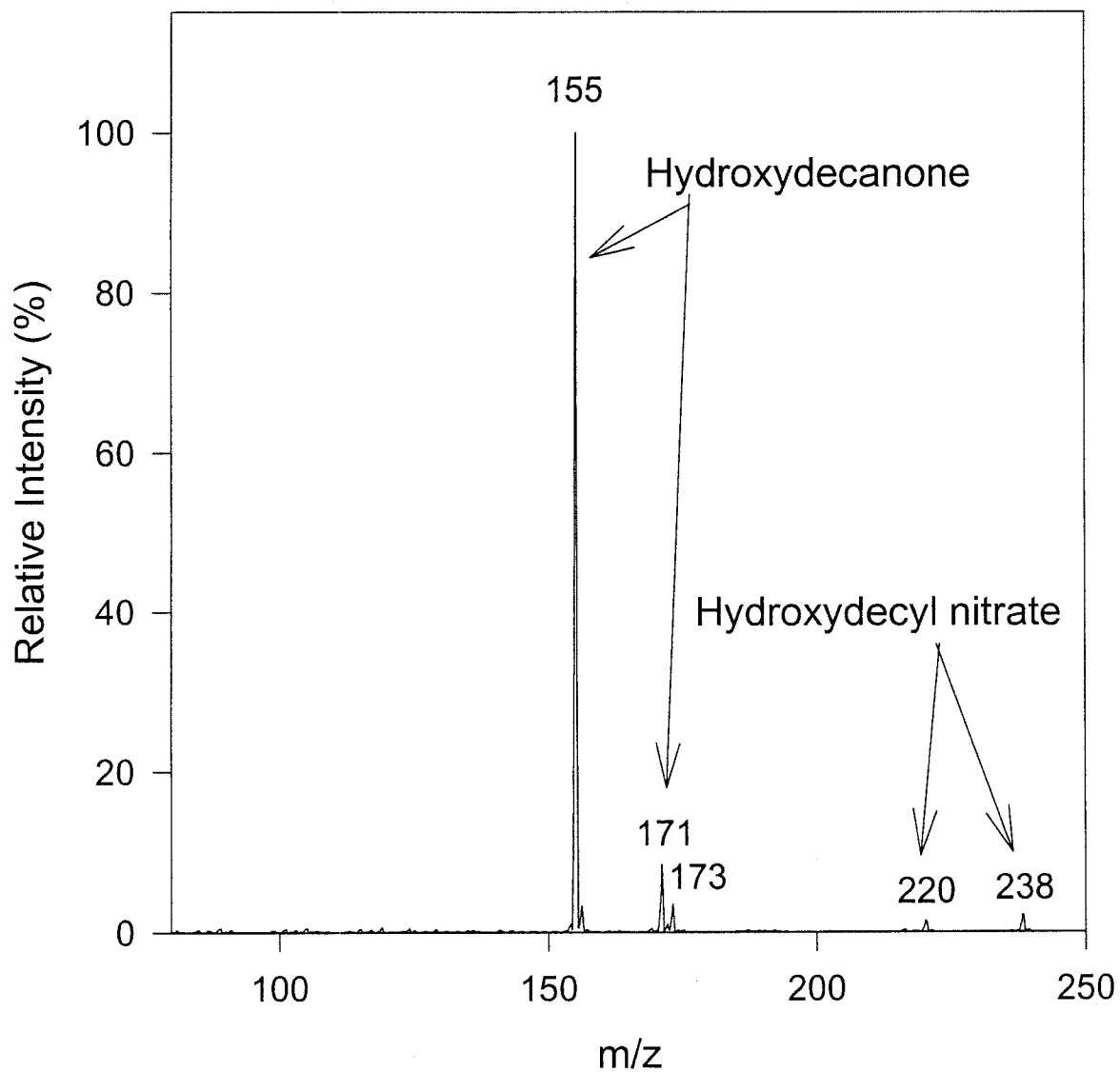
<sup>b</sup>Nolting *et al.* (1988).

<sup>c</sup>Behnke *et al.* (1988).

## *n*-Decane

- GC analyses showed the presence of 2-, 3-, 4- and 5-decyl nitrate. No other products were observed by GC analyses.
- API-MS analyses in positive ion mode showed the presence of products of MW 172 ( $C_{10}$ -hydroxycarbonyls), 203 (decyl nitrates) and 219 (hydroxydecyl nitrates).
- API-MS analyses with  $NO_2^-$  showed the presence of products of MW 172 ( $C_{10}$ -hydroxycarbonyls) and 219 (hydroxydecyl nitrates).

API-MS positive ion spectrum of OH  
radical-initiated reaction of *n*-decane



Products observed and their yields (%):

product	GC-FID	API-MS
decyl nitrates	$22.6 \pm 3.8$	obs
hydroxycarbonyls		obs, 22%
hydroxynitrates		obs, 2.4%

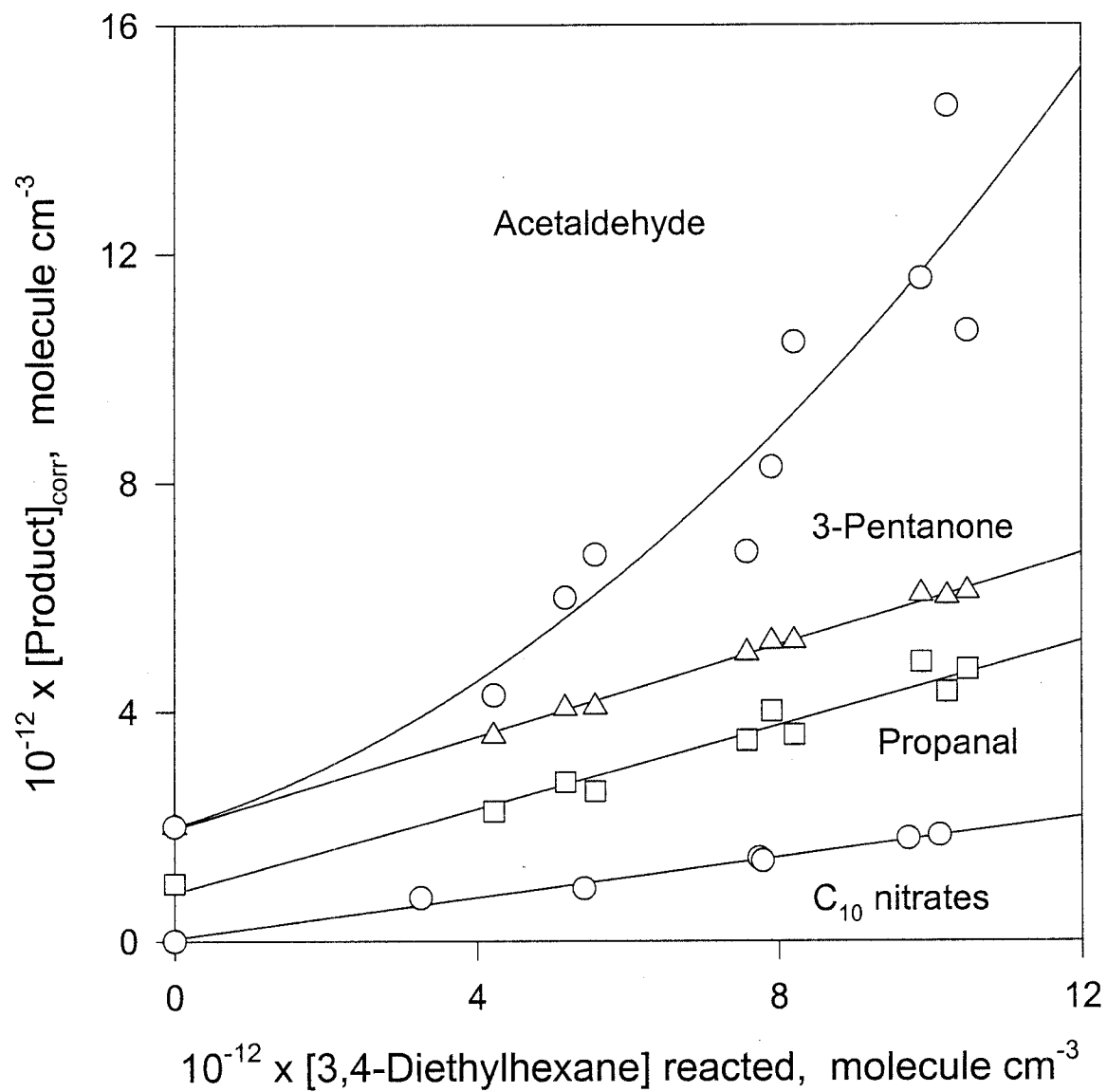
OH + 3,4-Diethylhexane and *n*-Butylcyclohexane

GC analyses showed C<sub>10</sub> alkyl nitrates from both alkanes,  
plus:

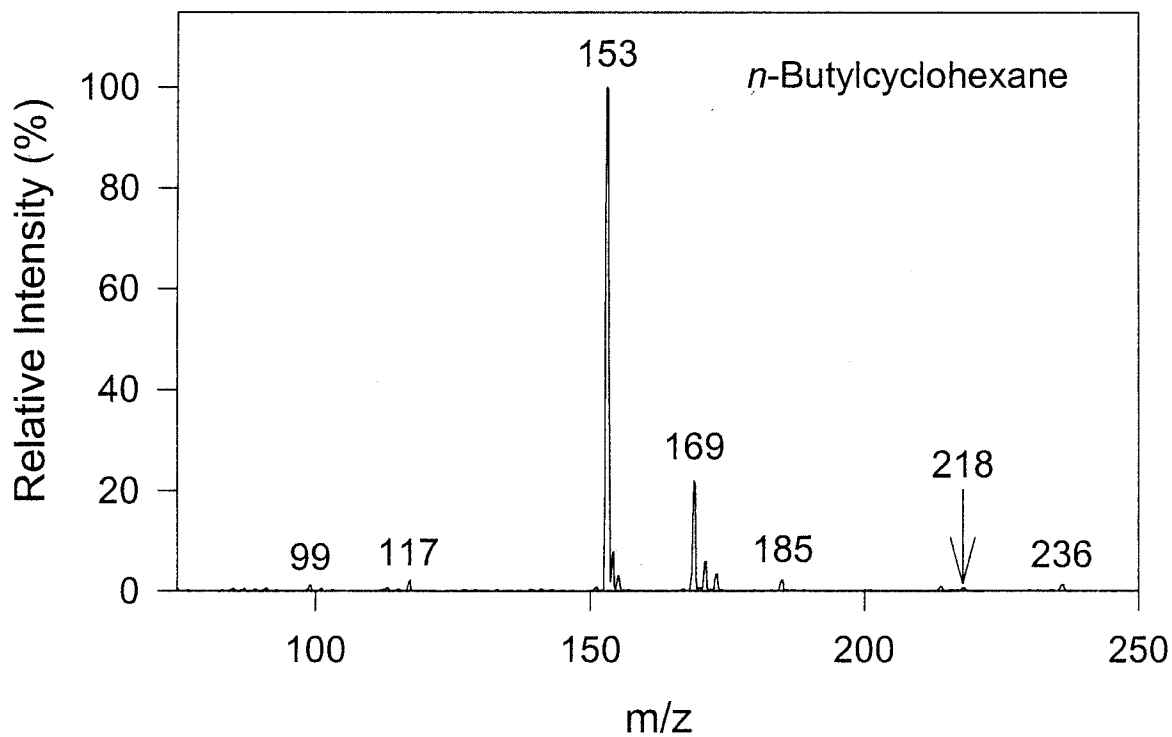
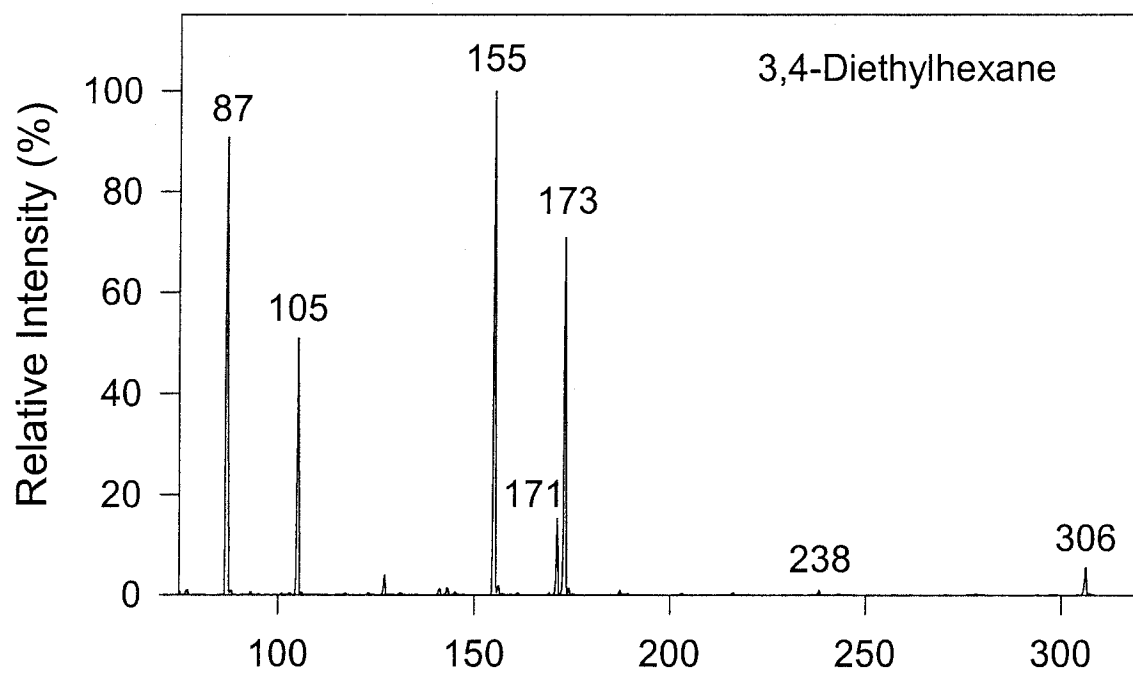
- Acetaldehyde, propanal, 3-pentanone and 3-pentyl nitrate from 3,4-diethylhexane.
- Propanal, butanal and cyclohexanone from *n*-butylcyclohexane.

API-MS analyses also showed presence of  
hydroxycarbonyls and hydroxynitrates.

OH + 3,4-diethylhexane, GC-FID analyses



API-MS analyses, positive ion mode



### 3,4-Diethylhexane

Product	GC-FID	API-MS
acetaldehyde	40%	
propanal	$37 \pm 6\%$	obs
3-pentanone	$40 \pm 4\%$	obs
3-pentyl nitrate	$2.3 \pm 1.1\%$	
C <sub>10</sub> -nitrates	$17.7 \pm 3.2\%$	
hydroxycarbonyls		obs, 11%
hydroxynitrates		obs, 1.7%

*n*-Butylcyclohexane

Product	GC-FID	API-MS
propanal	$\leq 5\%$	
butanal	$7.2 \pm 0.9\%$	obs
cyclohexanone	$4.9 \pm 0.7\%$	obs
C <sub>10</sub> -nitrates	$19 \pm 6\%$	
hydroxycarbonyls		obs, 37%
hydroxynitrates		obs, 2.3%

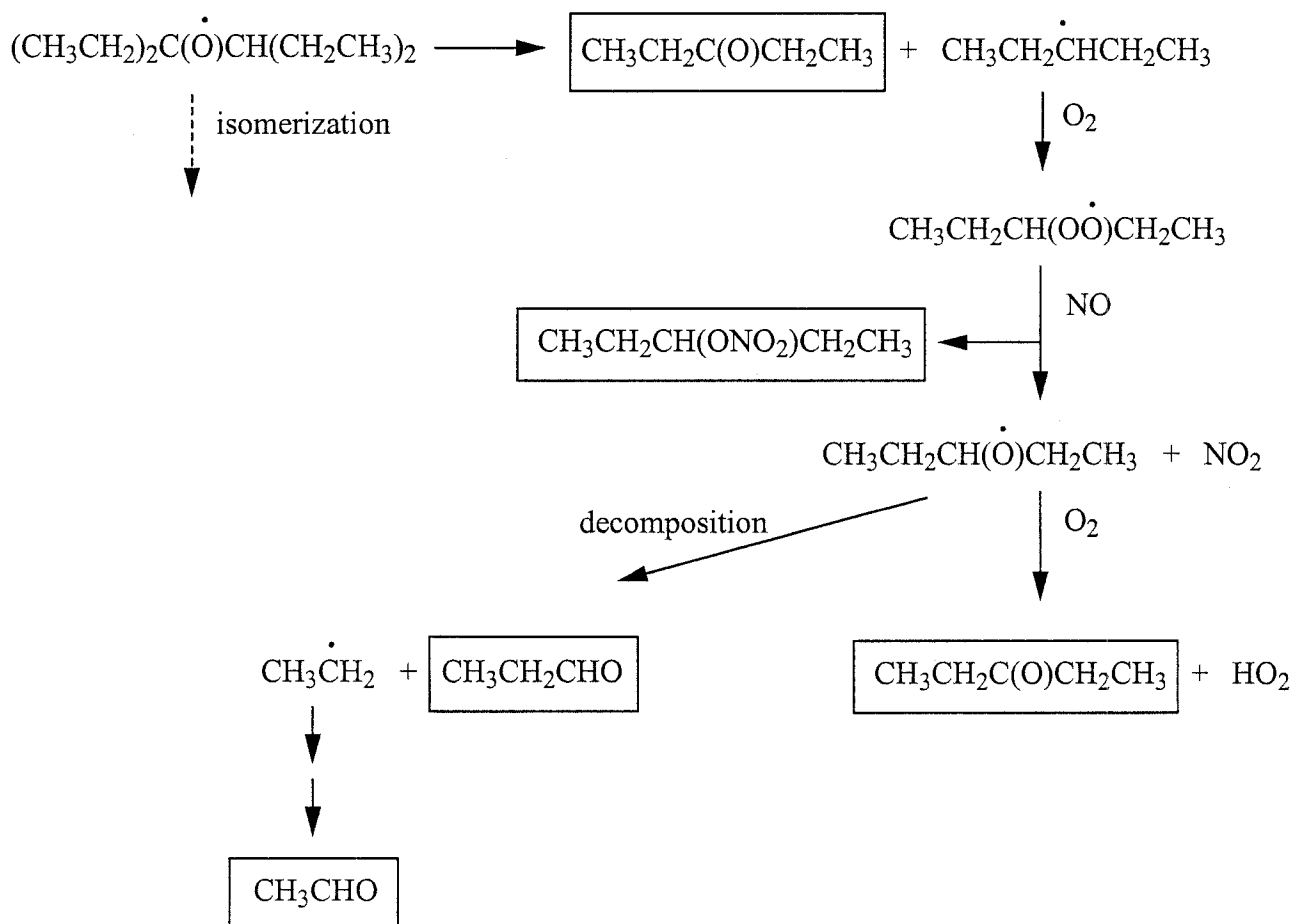
Product formation yields from reactions of the OH radical with a series of C<sub>5</sub>-C<sub>10</sub> alkanes studied in our laboratory, in the presence of NO.

alkane	Yield (%) of gas-phase products			
	Carbonyls	Alkyl nitrates	Hydroxycarbonyls	Hydroxynitrates
<i>n</i> -pentane	47	10.5	36	2.6
<i>n</i> -hexane	10	14.1	53	4.6
<i>n</i> -heptane	≤1	17.8	46	4.7
<i>n</i> -octane	≤1	22.6	27	5.4
<i>n</i> -decane		22.6	22	2.4
2,2,4-trimethylpentane	40		11	
3,4-diethylhexane	~40	18	11	1.7
<i>n</i> -butylcyclohexane	7	19	37	2.3

## CONCLUSIONS

If alkoxy radical isomerization can occur, then hydroxycarbonyls and hydroxynitrates will be formed. This is the case for *n*-alkanes larger than *n*-hexane.

For branched alkoxy radicals, isomerization may not be feasible or may be slower than decomposition, in which case smaller carbonyls are formed.



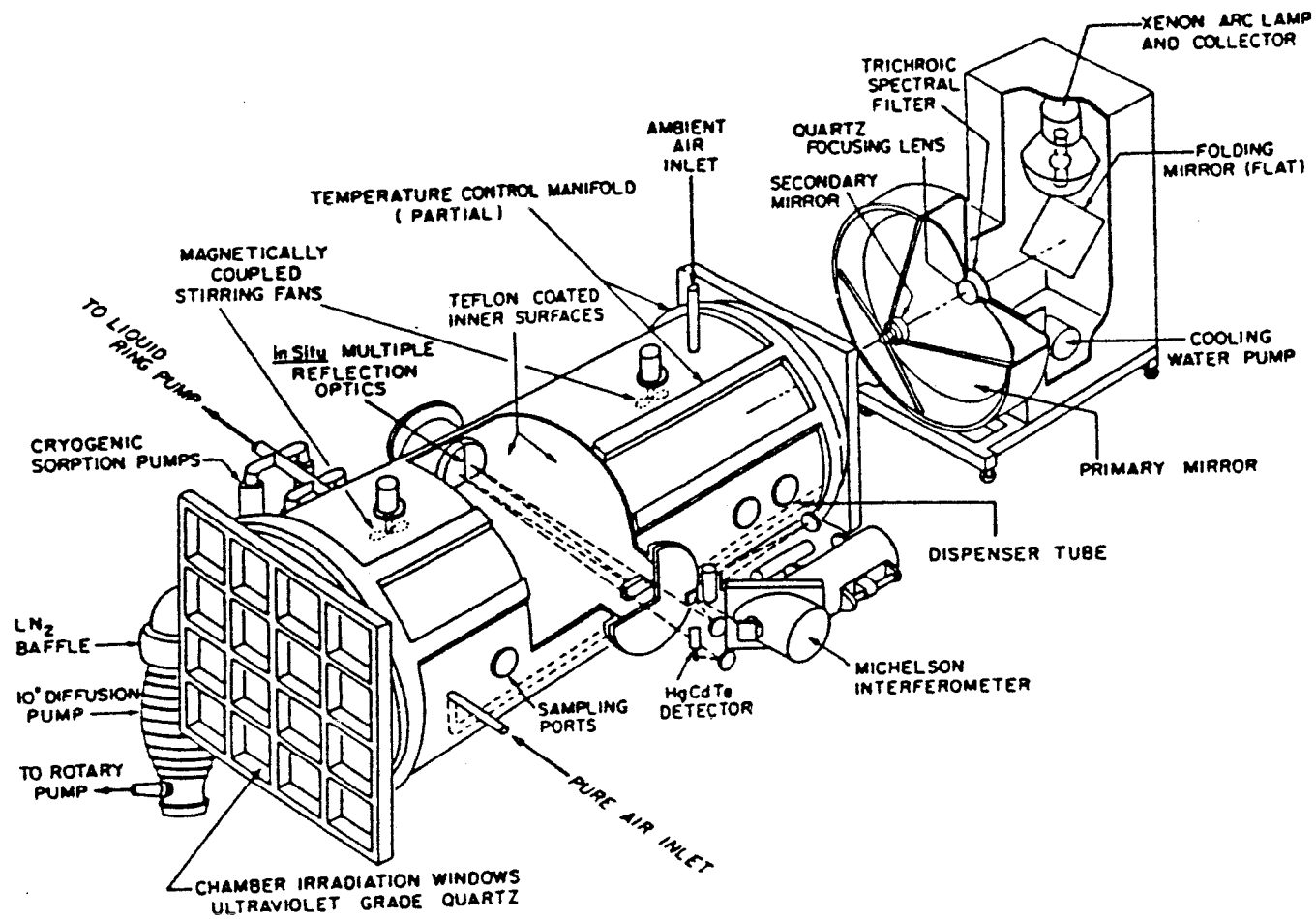
The “first-generation” products of the atmospheric reactions of alkanes are:

- Carbonyls
- Hydroxycarbonyls
- Alkyl nitrates
- Hydroxyalkyl nitrates

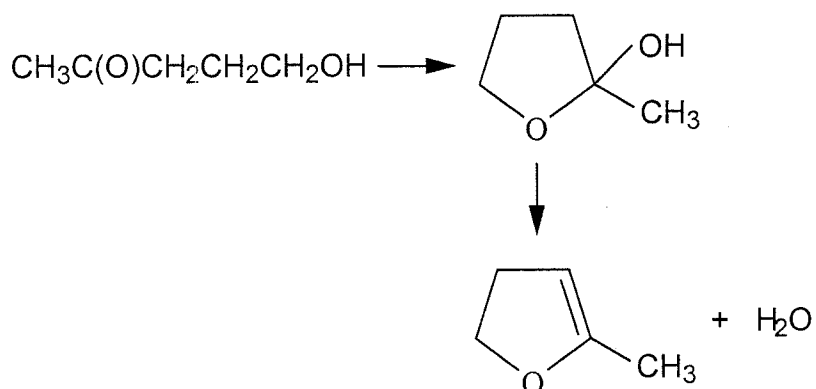
with 1,4-hydroxycarbonyls being formed in high yield in many cases. The only commercially available 1,4-hydroxycarbonyl is:

5-hydroxy-2-pentanone     $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

We have studied its reactions using primarily *in situ* FT-IR spectroscopy.



In dry air (<1% RH), 5-hydroxy-2-pentanone was observed to decay with a lifetime of 1.1 hr and forming 4,5-dihydro-2-methylfuran.



Therefore, we have investigated the atmospheric chemistry of 4,5-dihydro-2-methylfuran.

Rate constants and calculated lifetimes for the reactions of 4,5-dihydro-2-methylfuran with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> at 298 ± 1 K.

Reaction and reference compound	$k_1/k_2$	$k_1$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	Lifetime <sup>a</sup>
OH Reaction			
Cyclohexene	3.22 ± 0.32	(2.18 ± 0.31) × 10 <sup>-10</sup>	1.3 hr
2-Methylpropene	4.24 ± 0.22	(2.17 ± 0.24) × 10 <sup>-10</sup>	
		(2.18 ± 0.20) × 10 <sup>-10</sup>	
NO <sub>3</sub> Reaction			
2,3-Dimethyl-2-butene	2.94 ± 0.20	(1.68 ± 0.52) × 10 <sup>-10</sup>	24 s
O <sub>3</sub> Reaction			
2,3-Dimethyl-2-butene	3.09 ± 0.21	(3.49 ± 0.90) × 10 <sup>-15</sup>	7 min

<sup>a</sup>Calculated using 24-hour average tropospheric concentrations (molecule cm<sup>-3</sup>) of: OH radicals, 1.0 × 10<sup>6</sup>; NO<sub>3</sub> radicals, 2.5 × 10<sup>8</sup>; and O<sub>3</sub>, 7.4 × 10<sup>11</sup>.

Analyses of irradiated  $\text{CH}_3\text{ONO}$  – DMHF – air and  $(\text{CH}_3)_2\text{CHONO}$  – DHMF – air mixtures, using *in situ* FT-IR and API-MS analyses and GC-MS analyses, indicated the formation of an ester of molecular weight 116.

This is attributed to  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CHO}$

Based on measured IR absorption cross-sections of a series of esters,  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CHO}$  was quantified by FT-IR.

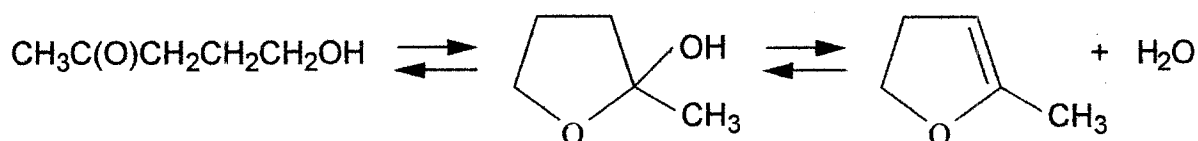
Products and their yields (corrected for secondary reaction) from  $\text{OH} + 4,5\text{-dihydro-2-methylfuran}$ .

Product	Molar yield (%)
$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CHO}$	$74 \pm 19$
HCHO	5.4 to 12
$\text{CH}_2=\text{CH}_2$	3.4 to 4.8
$\text{RC}(\text{O})\text{OONO}_2$	Secondary product

HOWEVER:

In contrast to the dry ( $\ll 1\%$  RH) system, *in situ* FT-IR analyses in the presence of water vapor ( $4.0 \times 10^{16}$  molecule  $\text{cm}^{-3}$ ; 5% RH) showed decay of 4,5-dihydro-2-methylfuran, with a lifetime of 3.5 hr and formation of 5-hydroxy-2-pentanone in  $\sim 90\%$  yield.

Therefore:



and the situation becomes more complex and involves the interconversion of 5-hydroxy-2-pentanone and 4,5-dihydro-2-methylfuran and concurrent reactions of both species.

Note that 5-hydroxy-2-pentanone is expected to be less reactive than 4,5-dihydro-2-methylfuran, by a factor of  $\sim 10$  for the OH radical reaction, by a factor of  $\sim 10^5$  for the  $\text{NO}_3$  radical reaction, and with no reaction with  $\text{O}_3$  expected.

## Related ongoing research at APRC

- We have shown that hydroxycarbonyls can be analyzed using a Solid Phase Micro-Extraction (SPME) fiber coated with pentafluorobenzylhydroxylamine hydrochloride, with *in situ* derivatization of carbonyl groups to form the oximes which are then analyzed by GC-FID and/or GC-MS.
- We have used this technique to observe 5-hydroxy-2-pentanone from the *n*-pentane reaction, 2 hydroxycarbonyls from the *n*-hexane reaction, and 3 from each of the *n*-heptane and *n*-octane reactions.
- We are using this technique to determine a rate constant for  $\text{OH} + 5\text{-hydroxy-2-pentanone}$ .